Glass and Ceramics, Vol. 68, Nos. 1 – 2, May, 2011 (Russian Original, Nos. 1 – 2, January – February, 2011)

SCIENCE FOR GLASS PRODUCTION

UDC 666.221:541.53

EQUILIBRIUM OF OXIDE FORMS OF CHROMIUM IN COLORED OPTICAL SILICATE GLASSES

A. B. Atkarskaya[1]

Translated from *Steklo i Keramika*, No. 2, pp. 3 – 7, February, 2011.

The formation of the equilibrium Cr(III) ↔ Cr(VI) in colored optical glasses under the combined effect of acid-base properties of the matrix, the total concentration of chromium, and the amount of other variable-valence elements which are in the oxidation – reduction series to the right of chromium is examined. It is shown that this equilibrium is related with the change of the spectral characteristics of the glass.

Key words: colored optical glass, oxidation-reduction equilibrium of chromium, basicity of glass, color transmission of glass, absorption coefficient.

Colored optical glass is used for developing light filters in instrument building instrument that select or cut-off a definite range in the visible and near IR and UV ranges of the spectrum. In the group of glasses colored yellow (YG), yellow-green (YGG), green (GG), and infrared (IRG), the required spectral characteristics are obtained by introducing into the mix copper oxides or chromium oxide in combination with copper and manganese oxides. These colored glasses are obtained in the system $R_2O – RO – SiO_2$, where R_2O denotes potassium and sodium oxides, RO — CaO, BaO, ZnO, and MgO [1]. The molar content of lead oxide does not exceed 5%; the PbO content is 35% only in YGG-19. Up to 4% B_2O_3 and 0.1% As_2O_3 (molar content) are introduced into individual compositions in order to adjust the technological and service properties.

To obtain a quantitative evaluation of the absorption intensity of any colored element in glass the specific absorption coefficient (SAC) χ_λ of the element is calculated as

$$\chi_{\lambda,\,\mathrm{Fe}} = \frac{-\log \tau_\lambda - 2D_{\rho m}}{l m_{\mathrm{Fe(total)}}}, \tag{1}$$

where τ_λ is the light transmission of the glass samples in units starting with 1; $D_{\rho m}$ is the correction for reflection; l is the thickness of the sample, cm; and, $m_{\mathrm{Me(total)}}$ is the mass content of the coloring element in the glass in terms of the metal, %.

The correction to $D_{\rho m}$ is calculated from the relation [2]

$$D_{\rho m} = -2\log(1 - r). \tag{2}$$

The scattering index r is related with the refractive index n of glass by the following relation [2]:

$$r = \frac{(n-1)^2}{(n+1)^2}. \tag{3}$$

Chromium, copper, and manganese belong to the family of d elements, and in silicate glass they coexist in two valence forms: Cr(III) and Cr(VI), Cu(I) and Cu(II), Mn(II) and Mn(III). The spectral curves of their specific absorption coefficient χ_λ are presented in Fig. 1 [3]. We note that univalent copper and bivalent manganese do not absorb in the visible and near regions of the spectrum. The Cu(II) ion forms two complexes with oxygen: quadruply coordinated "yellow" $[Cu(II)O_4]$ absorbs in the short-wavelength region and "blue" $[Cu(II)O_6]$ possesses a strong band in the 750 – 800 nm region.

Figure 1 shows that the course of the spectral curve and the light transmission of the glass colored by chromium alone or in combination with copper and manganese should depend strongly on the relation between the oxide forms of these elements, i.e., on the equilibria Cr(III) ⇄ Cr(VI), Cu(I) ⇄ Cu(II), and Mn(II) ⇄ Mn(III).

The equilibrium between the oxidized and reduced forms of the d elements in glass has been studied in greatest detail for iron and depends on many parameters of the technological process: the amount of the d elements, the acid-base

[1] Affiliate of the V. G. Shukhov Belgorod State Technological University, Novorossiisk, Russia (e-mail: atkarsk06@mail.ru).

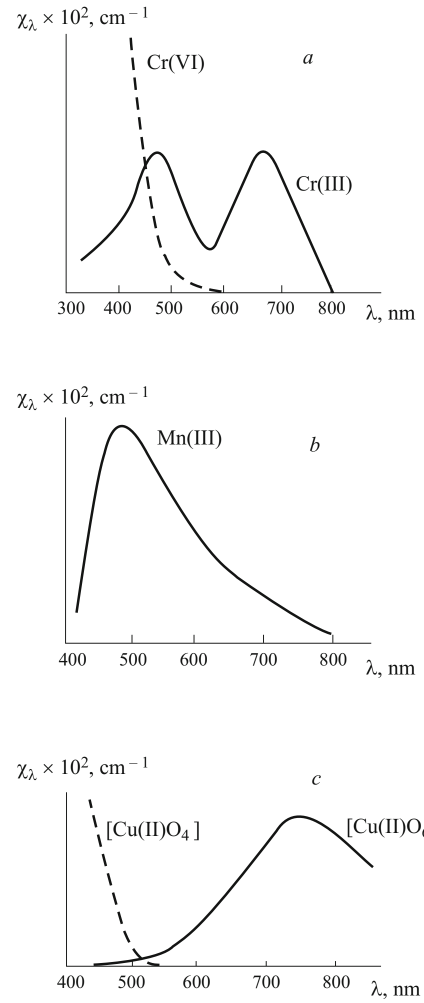

Fig. 1. Spectral curves of the specific absorption coefficients of chromium (*a*), manganese (*b*), and copper (*c*) in silicate glasses.

properties of the glass matrix, the oxidation – reduction and temperature – time regimes of glassmaking and extraction, the anionic composition of the raw materials for introducing alkali and alkali-earth components into the mix, and the presence and concentration of other variable-valence elements [4].

The present work is concerned with the formation of chromium equilibrium in colored optical silicate glasses obtained under commercial production conditions. The main objective is to determine the trend of the change of the chromium equilibrium under the combined effect of several technological factors, since the existing data are insufficient for a complete and comprehensive analysis.

As the content of the basic oxides increases and that of the acidic oxides decreases the coloring elements with variable valence tend to increase the degree of oxidation and vice versa [5]. The basicity K_{base} [6] calculated according to the following expression was used to obtain a quantitative evaluation of the acid-base properties of the matrix:

$$K_{\text{base}} = \frac{4.6Al_2O_3 + 4.7(K_2O + Na_2O + BaO + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)}{0.82SiO_2 + [B_2O_3 - (K_2O + Na_2O + BaO + 0.3ZnO + 0.7CaO + 0.7PbO - Al_2O_3)]},$$

where SiO_2, B_2O_3, Al_2O_3, K_2O, Me_2O, MeO, and so on are, respectively, the molar content of the oxides of silicon, boron, aluminum, alkali-, and bivalent metals, %.

When several elements with variable valence are present in the glass at the same time they affect one another via the Weil oxidation – reduction series presented below (5) [3, 5]. Each oxide appearing on the left-hand side is capable of oxidizing in a higher valence form any lower-valence oxide appearing on the right-hand side:

$$\begin{gathered} CrO_3 \rightleftarrows Mn_2O_3 \rightleftarrows CeO_2 \rightleftarrows CuO \rightleftarrows \\ As_2O_5 \rightleftarrows Sb_2O_5 \rightleftarrows Fe_2O_3; \\ Cr_2O_3 \rightleftarrows MnO \rightleftarrows Ce_2O_3 \rightleftarrows Cu_2O \rightleftarrows \\ As_2O_3 \rightleftarrows Sb_2O_3 \rightleftarrows FeO. \end{gathered} \tag{5}$$

For quantitative evaluation of the effect of manganese, copper, and arsenic on the equilibrium of chromium we introduce the concept of their "reduced concentration" γ calculated from the expression

$$\gamma = \frac{C_{\text{As}} + C_{\text{Mn}} + C_{\text{Cu}}}{C_{\text{Cr}}}, \tag{6}$$

where C_{As}, C_{Mn}, C_{Cu}, and C_{Cr} are the contents, in wt.%, of arsenic, manganese, copper, and chromium, in the glass according to synthesis in terms of the metal.

The physical meaning of the value of γ is the total content, per 1 wt.% chromium, of the variable-valence elements, which lie in the Weil oxidation-reduction series (5) farther to the right and for this reason have a reducing effect on Cr.

The glasses studied and some of their characteristics are presented in Tables 1 – 3. The content by weight of tri- and hexavalent chromium was calculated using the spectral curve of the glass and the spectrometric method [7], based on the Bouguer – Lambert – Beer rule, according to which when several colorants are present simultaneously the absorption coefficient a_λ of the glass for any wavelength $_\lambda$ is equal to the sum of the products of the specific absorption index χ_λ and content by weight C of each ion in the glass, i.e., $a_\lambda = \Sigma\chi_\lambda C$.

For a quantitative evaluation of the positions of the equilibrium Cr(III) ⇄ Cr(VI) the expression (7) was used to calculate the relative fraction α of the trivalent (or hexavalent) chromium with respect to the total amount of chromium introduced into the glass:

$$\alpha = \frac{C_{\text{Cr(III)}}}{C_{\text{Cr}}} \times 100\%, \tag{7}$$

where $C_{\text{Cr(III)}}$ and C_{Cr} are the content by weight, %, of the trivalent (as calculated) and total (according to synthesis) chromium in terms of the metal, respectively.

Table 1 shows four glasses, the spectral curve and the light-transmitting element whose absorption is formed by a

TABLE 1. Some Characteristics of Chromium-Colored Glasses

Glass designation	K_{base}	According to synthesis			Computed data				γ
		Content of added elements, wt.%			a, %		Content, wt.%		
		As	F	Cr	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
ZhS-3	3.99	0	0.48	0.017	37	63	0.007	0.010	0
ZhZS-19	5.82	0	0	0.051	28	72	0.014	0.037	0
ZhZS-5	3.13	0.227	0	0.089	77	23	0.069	0.020	2.56
ZhZS-6	3.12	0.227	0	0.179	68	32	0.122	0.057	1.27

TABLE 2. Some Characteristics of Glasses Colored with Chromium and Copper

Glass designation	K_{base}	According to synthesis			Computed data				γ
		Content of added elements, wt.%			Content, wt.%		α, %		
		As	Cr	Cu	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
ZS-3	2.47	0	0.322	1.062	0.322	0	100.0	0	3.31
ZS-11	3.56	0	0.376	0.719	0.376	0	100.0	0	1.91
ZS-1	2.96	0.227	0.607	0.415	0.545	0.062	89.7	10.3	1.06
ZhZS-1	2.96	0.227	0.753	0.519	0.562	0.191	74.7	25.3	0.99
ZhZS-9	3.11	0.227	0.318	0.143	0.214	0.104	67.0	33.0	1.16

single coloring element — chromium. It is evident that the relative fraction α Cr(III) is lowest (28 – 36%) in the glasses YG-3 and YGC-19 because of the absence of arsenic oxide, which has a reducing effect on chromium in accordance with the series (5). In conformance to the rule, the increase of α is inversely proportional to the value of K_{rel} of the glass [3].

Arsenic oxide displaces the equilibrium Cr(III) $\rightleftarrows$ Cr(VI) leftward, and the relative fraction of Cr(III) in the glasses ZhS-5 and -6 increases two-fold: from 28 – 37 to 68 – 77%. Here the increase in α is proportional to the "reduced concentration" of arsenic.

In Table 2 two variable-valence elements — arsenic and copper — on the right-hand side of the series (5) act on chromium. The Cr(III) content by weight decreases systematically from 100 to 74.7% as γ decreases from 3.79 to 0.99. It should be noted that here the effect of the acid-base properties of the matrix on the chromium equilibrium is secondary, since in the ZhZS-9, ZS-1, and ZS-11 glasses with basicity varying from 2.47 to 3.56 the Cr(III) fraction remains the same and equal to 100%. But in the glasses ZC-1 and ZhZS-1 with the same K_{base} the trivalent chromium fraction differs by almost 15% because of the different values of γ.

Table 3 shows three glasses colored by a combination of chromium and manganese. The maximum 100% degree of reduction of chromium is reached in IKS-5 glass. We also note that according to calculations the Mn(III) fraction in this glass is also maximum and equals 100%, which is in complete agreement with the mutual affect of these elements one another.

An increase of K_{base} in IKS-1 and -3 as compared with IKS-5 from 1.98 to 2.10 and 2.65, respectively, as does the introduction of arsenic, intensifies the oxidation of chromium and lowers the value of α from 100 to 60 – 75%, respectively.

The results of studies of the 12 experimental glasses are generalized graphically in Fig. 2.

TABLE 3. Some Characteristics of Glasses Colored by Chromium and Manganese

Glass designation	K_{base}	According to synthesis			Computed data				γ
		Content of added elements, wt.%			Content, wt.%		α, %		
		As	Cr	Mn	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
IKS-1	2.65	0.236	0.298	1.365	0.222	0.076	74.6	25.4	5.37
IKS-5	1.98	0	0.342	1.044	0.342	0	100.0	0	3.05
IKS-3	2.10	0.249	0.985	5.173	0.592	0.393	60.0	40.0	5.50

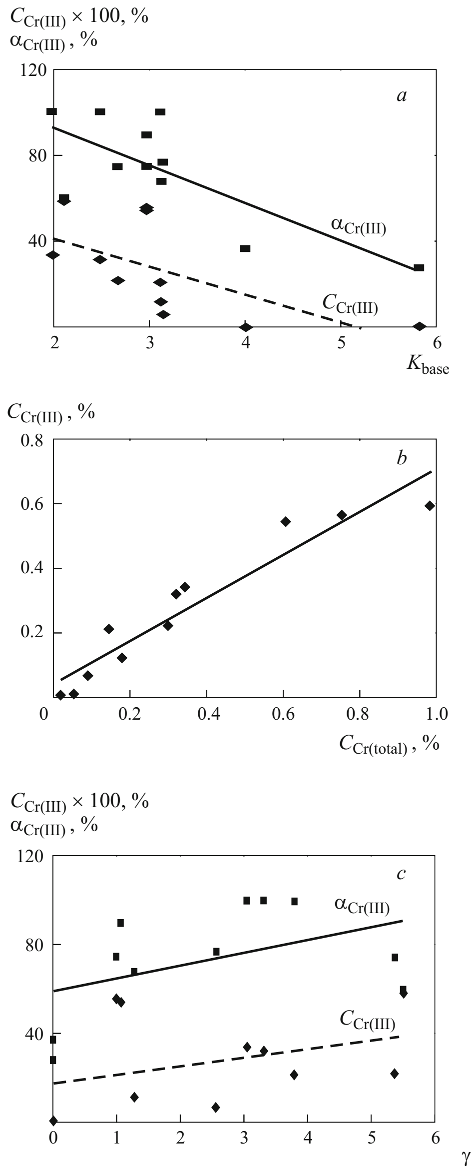

Fig. 2. Plots of the content C (wt.%) and fraction α of trivalent chromium versus K_{base} of glass (a), total chromium content (b), and "reduced" concentration γ of arsenic, manganese, and copper in glass (c).

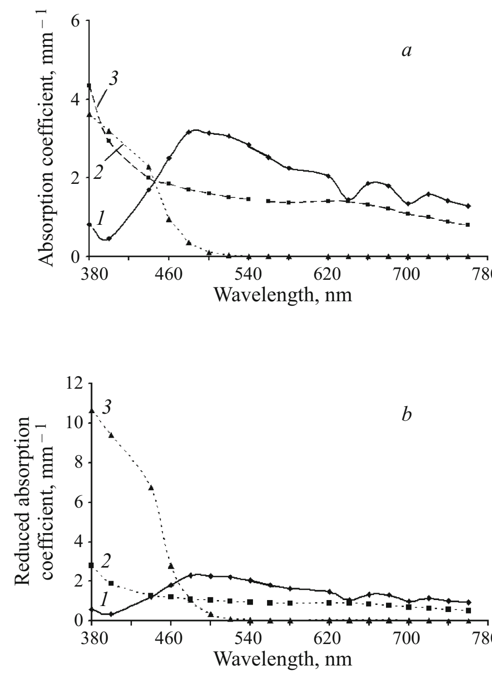

Fig. 3. Spectral curves of the average (a) and "reduced" average (b) absorption coefficients of glass. The numbers on the curves correspond to the numbers of the groups in Table 5 (in Fig. 3b the values of the "reduced" absorption coefficients of group-3 glasses are decreased by a factor of 10).

It is evident that the content (wt.%) and relative fraction of Cr(III) decrease with increasing basicity of the glass matrix (Fig. 2a) and increase with increasing total content of chromium (Fig. 2b) as well as the "reduced concentration" of γ copper, manganese, and arsenic (Fig. 2c).

The variance of the values in Fig. 2 is very large and is explained by the effect of additional factors, neglected in the present work, on equilibrium chromium. To confirm the reality of the behavior regularities observed in Table 4 all glasses studied were divided into two groups — those containing and not containing arsenic and those arranged in order of increasing values of K_{base}. It is evident from the data in Table 4 that in glasses colored by chromium or a combination of chromium with manganese and arsenic, a close correlation does indeed exist between the displacement of the equilibrium Cr(III) ⇄ Cr(VI) leftward, an increase of the acidic (decrease of basic) properties of the matrix and an increase of the "reduced" concentration of the variable-valence elements, located to the right of chromium in the oxidation-reduction series. Undoubtedly, this will have a decisive effect on the formation of the spectral curve of light transmission of colored glasses.

To confirm this supposition the change of the average values of the absorption coefficient $a_{\lambda,\,av}$ and the "reduced" average absorption coefficients $\bar{a}_{\lambda,\,av}$ of the glasses listed in Table 4 at wavelengths 400, 460, and 640 nm, corresponding or close to the maxima of the bands of hexavalent and trivalent chromium in silicate glass is shown in Table 5 (see Fig. 1). The reduced absorption coefficients make it possible to take account of the effect of the concentration of the coloring elements, which in colored glass of different designations differs very strongly (see Table 1 – 3).

The values of $a_{\lambda,\,i}$ for each glass are taken from [2], while $\bar{a}_{\lambda,\,i}$ were calculated from the expression

$$\bar{a}_{\lambda,i} = \frac{a_{\lambda,i}}{C_{(\mathrm{Cr+Mn+Cu}),\,i}}, \qquad (8)$$

where $C_{(\mathrm{Cr+Mn+cu}),\,i}$ is the total mass content of copper, chromium, and manganese in this glass (according to synthesis) in terms of the metal, %.

TABLE 4. Some Properties of the Experimental Glasses

Group	Designations of glasses in a group	K_{base}	Average content							γ
			Content of added elements, wt.%			Calculation				
			As	Cr	Cu or Mn	Content, wt.%		a, %		
						Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
1	IKS-5, ZS-3	2.23	0	0.332	1.053	0.332	0	100.0	0	3.18
2	IKS-1, IKS-3, ZS-1, ZhZS-1, ZhZS-9, ZhZS-5, ZhZS-6	2.86	0.231	0.436	1.113	0.332	0.114	77.7	22.3	2.93
3	ZhS-3, ZhZS-19	4.91	0	0.034	0	0.011	0.024	32.5	67.5	0

TABLE 5. Average "Reduced" Absorption Coefficients of the Experimental Glasses

Group	Designation of glasses in a group	Average "reduced" absorption coefficient, mm^{-1} at wavelength, nm		
		400	460	640
1	ZS-3, IKS-5	0.335740	1.808664	1.046931
2	ZS-1, ZhZS-9, ZhZS-1, ZhZS-5, ZhZS-6, IKS-1, IKS-3	1.897076	1.197086	0.906391
3	ZhZS-19, ZhS-3	93.97059	28.029410	0.514706

The coefficients $a_{\lambda,\,av}$ and $\bar{a}_{\lambda,\,av}$ in each group of glasses were obtained by averaging concrete values, for example,

$$a_{\lambda,\,av} = \frac{\sum a_{\lambda,i}}{n},$$

where n is the number of glasses in the group studied.

Evidently, on passing from the first to third group the average "reduced" absorption coefficient increases at the wavelength 400 nm and decreases at 640 nm. We recall that hexavalent chromium absorbs in the short-wavelength region of the spectrum while hexavalent chromium has two bands in the visible part of the spectrum — near 460 and 640 nm. For this reason, the change of the values of $\bar{a}_{\lambda,\,av}$ confirms that the chromium equilibrium in the first group is displaced in the direction of the trivalent equilibrium and in the third group to the hexavalent form. The curves in Fig. 3 indicate a close relation between the absorption spectra of colored glasses and the equilibrium in them of the oxide forms of chromium: glasses in the first and second groups attenuate to different degrees the transmission of the visible wavelength range, while group-3 glass effectively "cuts off" the radiation in the blue and adjoining visible parts of the spectrum.

On this basis it can be concluded that in chromium-colored optical glasses the equilibrium Cr(III) $\rightleftarrows$ Cr(VI) is displaced leftward as the acidic properties of the matrix increase (basic properties decrease) and the "reduced" concentration of the variable-valence elements lying to the right of chromium in the oxidation – reduction series increases. At the same time the glasses in which Cr(III) predominates attenuate the visible light transmission while Cr(VI) effectively "cuts off" the radiation in the blue and adjoining visible parts of the spectrum.

REFERENCES

1. *OST 3-4375–79. Optical Colored Glass. Synthetic Composition. In place of NO 2752–69. Introduced July 1, 1981* [in Russian], Izd. GOI, Leningrad (1979).
2. G. T. Perovskii, *Catalogue of Colored Optical Glass and Special Glasses* [in Russian], Moscow (1990).
3. L. I. Demkina, *Physical-Chemical Principles of the Production of Optical Glass* [in Russian], Khimiya, Leningrad (1976).
4. N. I. Min'ko, "Effect of the oxidation – reduction potential of a mix based on the glassmaking processes and the properties of glass," in: *Selected Works* [in Russian], Izd. BGTU im. V. G. Shukhova, Belgorod (2004), pp. 23 – 32.
5. V. V. Vargin, *Production of Colored Glass* [in Russian], Gos. Izd. Legkoi Promyshlennosti (1940).
6. M. V. Artamonova, V. I. Kiyan, and Yu. I. Mashir, "Evaluation of the acid-base properties of sodium aluminoborosilicate glasses," *Fiz. Khim. Stekla*, **12**(6), 731 – 739 (1986).
7. OST 3-4728–79. *Colored Optical Glass. Spectrometric Method of Determining the Content of Coloring Impurities* [in Russian], GOI, Leningrad (1979).